MEMORANDUM
RM-4128-PR
MAY 1964

12-p- $0.50

ON THE BEHAVIOR OF A CHEMICAL EQUILIBRIUM SYSTEM WHEN ITS FREE ENERGY PARAMETERS ARE CHANGED

N. Z. Shapiro

PREPARED FOR:
UNITED STATES AIR FORCE PROJECT RAND

The RAND Corporation
SANTA MONICA • CALIFORNIA

MEMORANDUM

RM-4128-PR

MAY 1964

ON THE BEHAVIOR OF A CHEMICAL EQUILIBRIUM SYSTEM WHEN ITS FREE ENERGY PARAMETERS ARE CHANGED

N. Z. Shapiro

This research is sponsored by the United States Air Force under Project RAND—contract No. AF 49(638)-700 monitored by the Directorate of Development Planning, Deputy Chief of Staff, Research and Development, Hq USAF. Views or conclusions contained in this Memorandum should not be interpreted as representing the official opinion or policy of the United States Air Force.

The RAND Corporation

1700 MAIN ST. • SANTA MONICA • CALIFORNIA • 90406

PREFACE AND SUMMARY

One aspect of RAND work on the development of computer models to represent physiological subsystems is concerned with the resolution of attendant problems of theoretical and computational mathematics. In a previous Memorandum--Mass Action Laws and the Gibbs Free Energy Function, N. Z. Shapiro and L. S. Shapley, RM-3935-PR, December 1963--the use of the Gibbs free energy function vis-à-vis the mass action laws for the analysis of complex chemical systems was considered. The present Memorandum continues that discussion, obtaining an inequality concerning the effect on a chemical system of changing its free energy parameters.

INTRODUCTION

In this Memorandum we obtain an inequality which furnishes information about the behavior of a chemical equilibrium system when its free energy parameters are changed.

The result is proved by viewing the solution of a chemical equilibrium problem as the result of minimizing the free energy function. Were the solution viewed in terms of the mass action laws, the proof would become much more difficult.

ON THE BEHAVIOR OF A CHEMICAL EQUILIBRIUM SYSTEM WHEN ITS FREE ENERGY PARAMETERS ARE CHANGED

Theorem 1. Let P and $P^{\#}$ be chemical equilibrium problems* which are identical except possibly for their free energy parameter vectors, c and $c^{\#}$. (That is, P and $P^{\#}$ contain the same species, compartmentalized in the same way and obeying identical mass balance laws, $Ax = b$. In other words, $P^{\#}$ is the problem obtained from P by replacing c by $c^{\#}$.) Let x be any solution of P and let $x^{\#}$ be any solution of $P^{\#}$. (Note: We do not assume that P or $P^{\#}$ necessarily has a unique solution. Thus, x may be one of possibly many solutions of P.) (Note: We do not assume that x or $x^{\#}$ is positive; that is, some of their components may be zero.) It then follows that

$$x^{\#} \cdot (c^{\#} - c) \leq x \cdot (c^{\#} - c) \quad . \tag{1}$$

Furthermore, if $c^{\#}$-c is not representable as a linear combination of the rows of the constraint matrix A, and

---

*For a detailed introduction to the subject matter of this Memorandum, see Part I of RM-3935-PR, Mass Action Laws and the Gibbs Free Energy Function, N. Z. Shapiro and L. S. Shapley, December 1963, and also the publications referenced in that Memorandum.

if all the components of either x or of $x^{\#}$ (or of both x and $x^{\#}$) are positive, then

$$x^{\#} \cdot (c^{\#} - c) < x \cdot (c^{\#} - c) \ .$$

Before proving Theorem 1, we give two examples of applications of the theorem.

Example 1. If a chemical equilibrium problem with a solution x is altered by increasing one of the free energy parameters c_j, and if $x^{\#}$ is any solution of the resulting problem, then

$$x_j^{\#} \leq x_j \ .$$

Furthermore, if x is positive and if x_j is not determined solely by the mass balance constraints, then

$$x_j^{\#} < x_j \ .$$

Example 2. Let a chemical equilibrium problem, having a positive solution, x, be altered by increasing each of the c_j's in one of the compartments by the same positive

amount. (Note: This corresponds, loosely speaking, to increasing the pressure of that compartment.) Let $x^{\#}$ be any solution of the resulting problem. Let $\bar{x}$ and $\bar{x}^{\#}$ denote the sum of the x_j's and of the $x_j^{\#}$'s in the affected compartment. Then, if $\bar{x}$ is not determined solely by the mass balance constraints, we have

$$\bar{x}^{\#} < \bar{x} .$$

Theorem 1 follows from a more general result. To state this more general proposition: Let n be a positive integer. Let E^n be Euclidian n-dimensional space. Let H be a convex subject of E^n. Let H^0 be the interior of H relative to the linear manifold on E^n generated by H. Let F be a real-valued convex function defined on H.

If u is any element of H and if θ is any element of E^n such that $u + t\theta$ is an element of H for all sufficiently small positive real t, then the directional derivative $F_\theta'(u)$ is defined by

$$F_\theta'(u) = \lim_{t \to 0+} \frac{F(u+t\theta) - F(u)}{t} \tag{2}$$

It is well known that the convexity of F assures the existence (if we accept $-\infty$ as a limit) of $F'_\theta(u)$. It is also well known that if u and v are elements of H, then

$$F(v) - F(u) \geq F'_{v-u}(u) . \tag{3}$$

We will say that F is <u>weakly differentiable</u> at a point u in H, if for all θ (for which $u + t\theta$ is in H for all real t with sufficiently small absolute values) for which $F'_\theta(u) \geq 0$ and $F'_{-\theta}(u) \geq 0$, we have

$$F'_\theta(u) = F'_{-\theta}(u) = 0 . \tag{4}$$

(Note: Weak differentiability follows from the stronger assumption that $F'_{-\theta}(u) = -F'_\theta(u)$ for all θ (for which $u + t\theta$ is in H for all t having sufficiently small absolute values).)

Let Δ be any element of E^n. Let $F^{\#}$ be a real-valued function defined on H by means of

$$F^{\#}(u) = F(u) + \Delta\cdot u . \tag{5}$$

Then, Theorem 1 will follow from:

Theorem 2. Let x be a member of the minimum set of F on H, and let $x^{\#}$ be a member of the minimum set of $F^{\#}$ on H. Then,

$$\Delta \cdot x^{\#} \leq \Delta \cdot x \ . \qquad (6)$$

Furthermore, if:

(A) F is weakly differentiable at x

(B) x is in H^0

(C) $\Delta \cdot u$ is not constant for all u in H

or if:

($A^{\#}$) F is weakly differentiable at $x^{\#}$

($B^{\#}$) $x^{\#}$ is in H^0

($C^{\#}$) $\Delta \cdot u$ is not constant for all u in H

then:

$$\Delta \cdot x^{\#} < \Delta \cdot x \ . \qquad (7)$$

Proof of Theorem 2. Let us first observe that for any u in H and for any θ for which $u + t\theta$ is in H for all sufficiently small positive t

$$F_{\theta}^{\#\,'}(u) = F_{\theta}'(u) + \Delta \cdot \theta \ . \tag{8}$$

In particular,

$$F^{\#\,'}_{x^{\#}-x}(x) = F'_{x^{\#}-x}(x) + \Delta \cdot (x^{\#}-x) \ . \tag{9}$$

But, since x is in the minimum set of F, we must have

$$F'_{x^{\#}-x}(x) \geq 0 \ . \tag{10}$$

But by (3)

$$F^{\#}(x^{\#}) - F^{\#}(x) \geq F^{\#\,'}_{x^{\#}-x}(x) \geq \text{(By (9) and (10))} \ \Delta \cdot (x^{\#}-x) \ . \tag{11}$$

But, since $x^{\#}$ is in the minimum set of $F^{\#}$, we have

$$F^{\#}(x^{\#}) \leq F^{\#}(x) \ ; \tag{12}$$

then, (6) follows (11) and (12).

To prove that (7) follows from (A), (B), and (C), or from ($A^{\#}$), ($B^{\#}$), and ($C^{\#}$), it would be sufficient (by the symmetry obtained when Δ is replaced by -Δ) to show that

(7) follows from (A), (B), (C).

Let us, therefore, assume (A), (B), and (C), and let us also assume that (7) is false. But, since we already proved (6), we have that

$$\Delta \cdot (x^{\#} - x) = 0 \ . \tag{13}$$

But this and (11), then, yield

$$F^{\#}(x^{\#}) \geq F^{\#}(x) \ , \tag{14}$$

so that (12) and (14) yield

$$F^{\#}(x^{\#}) = F^{\#}(x) \ . \tag{15}$$

Let u be a point in H guaranteed by (C) such that $\Delta \cdot u \neq \Delta \cdot x$. Let $\theta = u - x$. By (B), $x + t\theta$ is in H for all t with sufficiently small absolute values.

Since x is in the minimum set of F, we know that $F'_{\theta}(x) \geq 0$, and $F'_{-\theta}(x) \geq 0$. Hence, by (A)

$$F'_{\theta}(x) = F'_{-\theta}(x) = 0 \ .$$

Hence, by (8),

$$F^{\#'}_{\theta}(x) = \Delta\cdot\theta \quad \text{and} \quad F^{\#'}_{-\theta}(x) = -\Delta\cdot\theta \ .$$

Since $\Delta\cdot\theta \neq 0$, we have (if necessary by replacing θ by $-\theta$)

$$F^{\#'}_{\theta}(x) < 0 \ . \tag{16}$$

But, since $x^{\#}$ is in the minimum set of $F^{\#}$, (15) shows that x is in the minimum set of $F^{\#}$, a fact which contradicts (16). <u>QED</u>.